UNIVERSIDAD POLITÉCNICA DE CARTAGENA

ESCUELA DE INGENIERÍA DE CAMINOS, CANALES Y PUERTOS Y DE INGENIERÍA DE MINAS

TRABAJO FIN DE MASTER

ORGANIC MATTER DYNAMICS AND SOIL AGGREGATION IN A TECHNOSOL CREATED WITHMETALLIFEROUS MINE RESIDUES, BIOCHAR AND MARBLE WASTE

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INDEX

RESUMEN

Los objetivos de este estudio fueron determinar y explicar la influencia del biocarbón y residuos de mármol en dinámica de la materia orgánica y la agregación en una balsa de residuos en el distrito minero de Cartagena-La Unión (SE España). Tres tipos de biocarbón se obtuvieron a partir de estiércol de cerdo, residuos de depuradora municipal y residuos de cosecha hortícola a 500ªC durante 2 h. Ocho tipos de tratamientos fueron utilizados, que incluían: un suelo control (CT) sin la aplicación de enmienda, tres tratamientos con diferentes tipos de biocarbón, un tratamiento con los residuos de mármol y tres tratamientos con diferentes biocarbón más residuo de mármol. Se determinaron pH, conductividad eléctrica, agregados estables, carbono orgánico total, carbono inorgánico, carbono recalcitrante, carbono lábil, carbono soluble, nitrógeno total, nitrógeno recalcitrante, nitrógeno lábil, carbono de la biomasa microbiana, β-glucosidasa y actividad arilesterasa, hidrofobicidad, carbohidratos y emisiones de gases de efecto invernadero. Los resultados sugieren que el biocarbón, producido por diversas fuentes es una estrategia eficaz para secuestrar el carbono en el suelo y mejorar la estructura del mismo. Sin embargo, para recuperar de forma efectiva los residuos de mina sería necesario agregar una fuente lábil de materia orgánica con el fin de promover el desarrollo de las poblaciones microbianas.

Palabras clave: enmiendas, biocarbón, residuos de mármol, agregados estables, residuos mineros.

ABSTRACT

The objectives of this study were to determine and explain the influence of biochar and marble waste on soil organic matter dynamics and aggregation in tailings pond at the Mining District of Cartagena-La Union (SE Spain). Three types of biochars were obtained from pig manure, municipal soil waste andcrop residueat 500ªC during 2h. Eight types of treatmentswere used, which included: onesoil control (CT)without application of amendment, three treatments with different types of biochars, one treatment with marble waste and three treatments with different biocharsplus marble waste. pH, electrical conductivity, aggregation stability, total organic carbon, inorganic carbon, recalcitrant carbon, labile carbon, soluble carbon, total nitrogen, recalcitrant nitrogen, labile nitrogen, microbial biomass carbon, β-glucosidase and arilesterase activity, hidrofobicity, carbohidrates and greenhouse gas emissionswere determined. The results suggest that biochar, produced by diverse sources, is an effective strategy to sequester carbon in soil and improve soil structure. However, to effectively reclaim mine residues would be necessary to add a labile source of organic matter to promote the development of microbial populations.

Keywords: amendments, biochar, marble waste, aggregation stability, mine waste

1. INTRODUCTION

Metalliferous mine areas constitute degraded ecosystems resulting from mineral extraction for long periods of time, giving rise to large areas of derelict land. Environmental transformations related with mining activities entail changes in the morphology of the area owing to the extraction of minerals and dumping of residues, with reduction of vegetation cover and fauna diversity, and changes in soil quality and structure (Sadhu et al., 2012; Zawadzki et al., 2016).Metalliferous mine residues dumped into the environment have numerous restrictions affecting their development into natural soils, such as extremely low pH, high concentrations of metals and metalloids and extremely low organic matter content (Zanuzzi et al., 2009; Martínez-Pagán et al., 2011). These materials can also provoke acid mine drainage, a dangerous source of water contamination (Barrie and Hallberg, 2005).Therefore, there is a need to develop strategies to reduce the impact of mining residues spread on mine landscapes to guarantee ecosystem reclamation. One effective solution is the creation of Technosols (IUSS, 2014) by addition of different amendments, so that microorganisms and vegetation are able to colonize and grow. For this purpose, the proper selection of amendments to create soil structure is critical, since the most important processes for pedogenesis is the accumulation and cycling of soil organic matter and the formation of stable aggregates(Séré et al., 2010; Huot et al., 2014).

Organic residues are commonly used as amendments because the addition of organic matter can significantly improve soil structure and nutrient status(Senesi et al., 2007;Kayikcioglu, 2012).Biochar production through the pyrolysis of organic residues has recently become an interesting solution for successful soil reclamation due to its high recalcitrant carbon content, which can increase the content of stable organic carbon in soil, contribute to carbon sequestration, and improve soil physical, chemical and biological properties (Glaser et al., 2002; Lehman and Rondon, 2006; Marchetti et al., 2012). Biochar has also emerged as a strategy for reducing greenhouse gas(GHG) emissions. However, the effect of biochar on GHG highly depends on biochar feedstock and pyrolysis conditions, soil type and soil management (Cayuelaet al., 2010; Scheer et al., 2011;Taghizadeh-Toosi et al., 2012a,b; Harris et al., 2013). The importance of calcareous materials in supplying carbonates and Ca ions to neutralize acidity, contributing to buffer capacity and stabilize soil organic matter is well recognized (Stumm and Morgan, 1996; Calvet, 2013;Zornoza et al., 2013). For these reasons, several authors have suggested the use of marble wastes as a source of calcium carbonate for acidic soil remediation (Janjirawuttikul et al., 2011; Tozsin et al., 2014a; Zornoza et al., 2013).

Previous studies have reported the positive effects of Technosols created on mine and industrial residues through the addition of different amendments to ensure true landscape reclamation (Séré et al., 2010; Huot et al., 2014;Wiszniewsk, et al 2016).However, to really conclude that the addition of different organic and industrial wastes to mine residues efficiently contributes to soil creation, a proper and thorough monitoring of organic matter stability, GHG emissions, aggregation, and microbial biomass and activity should be developed. Since soil microorganisms are key in the stabilization and degradation of soil organic matter and in the formation of soil stable aggregates (Agegnehuet al., 2016;Zornoza et al., 2016a), the monitoring of microbial biomass and activity, and its interaction with soil physicochemical properties will help gain knowledge about microbial mediated processes in Technosols.

In order to elucidate the main factors controlling organic matter stabilization and degradation and soil aggregates formation in a Technosol derived from mine residues as strategy for reclamation, we performed a short-term incubation experiment with biochars derived from different feedstock and marble waste. Our objective was to assess the effects of the different amendments on the evolution of C and N pools, GHG emissions (CO_2, N_2O and CH_4), aggregate stability, and microbial biomass and activity. We hypothesized that the application of biochar and marble waste to mine soils can contribute to the stabilization of organic matter by formation of stable aggregates and the activation of microbial populations. Biochar type could have a strong influence on aggregate stability and microbial stimulation, while $CaCO_3$ may have a positive effect on aggregation by release of Ca^{2+} cations.

2. OBJETIVES

2.1 General objective

The objective of this study were to determine and explain the influence of biochar and marble waste on soil organic matter dynamics and aggregation in tailings pond at the Mining District of Cartagena-La Union (SE Spain).

2.2 Specific objectives

The different soils are periodically analyze to monitor the evolution of: pH, electrical conductivity, aggregate stability, total organic carbon, inorganic carbon, recalcitrant carbon, labile carbon, soluble carbon, total nitrogen, recalcitrant nitrogen, labile nitrogen, carbohydrates, microbial biomass carbon, β–glucosidase activity, arylesterase activity, hidrofobicity and greenhouse gas emissions (CO2, N2O and CH4) at 0, 2, 4, 7, 15, 30 and 90 days of incubation.

3. MATERIALS AND METHODS

3.1 Mine, organic and industrial residues used

A tailings pond at the Mining District of Cartagena-La Unión (SE Spain)(37°35'38’’ N, 0º53'11" W) was selected to collect the mine residues, which were characterized by high acidity andmet alloid concentrations, low organic carbon and nutrient contents, and sandy loam texture. The climate of the area is semiarid Mediterranean, with mean annual temperature of 18 ºC and mean annual rainfall of 275 mm. The mine residue was collected from the top 20 cm of the tailings pond, air-dried for seven days, and sieved <4mm for incubation experiments.

Biochar feedstock was pig manure (PM), cotton (*GossipiumhirsutumL.*) crop residues (CR) and municipal solid waste (MSW), collected in a pig farm, agricultural field and municipal solid waste treatment plant from the municipality of Cartagena (SE Spain). The feedstock was dried at 60 ºC in a forced air lab oven during 72 h and then was ground to pass a 4-mm sieve. The ground particles were then pyrolyzed in a muffle furnace. The temperature was increased at 5 ºC min-^{1} to 500 ºC and then maintained for 2 h at this temperature for each feedstock type. Biochar was then ground at < 250 µm for laboratory incubations. The marble waste (MaW; formed by particles of 5-10 µm diam.) was collected from quarries in the Northwest of the Region of Murcia(SE Spain). The main characteristics of all residues used are shown in Table 1 (Annex I).

3.2 Soil incubation

Eight different treatments were applied to the mine residue: unamendment mine residue used as control(CT), PM, CR, MSW, MaW, PM+MaW, CR+MaW and MSW+MaW. Biochars were thoroughly mixed with the mine residue at a dose of 20 g C kg^{-1} soil, which is the organic C content in the native shrubland soils of the area (Martinez-Martinez et al., 2013).The MaW was added in a rate of 50 g kg^{-1}. This rate was calculated using the method proposed by Sobek et al. (1978), which specifies the amount of $CaCO_3$ required to neutralize the acidification potential of the soil, according to the percentage of sulfides present in the mine residue, to reach a final pH of eight, which is the pH value in the native shrubland soils of the area (Martinez-Martinez et al., 2013).

Laboratory incubation (three replicates per treatment) was performedin plastic pots kept in the dark, to a constant humidity of 50% of water holding capacity and temperature of 22 ºC under aerobic conditions during 90 days. Soil moisture levels were gravimetrically maintained adding deionized water if needed. Technosols were sampled to monitor the evolution of pH, electrical conductivity (EC), aggregate stability (AS), total organic carbon(TOC), inorganic carbon (IC), recalcitrant carbon (Crec), labile carbon (Clab), soluble carbon (Csol), total nitrogen (Nt), recalcitrant N (Nrec), labile nitrogen (Nlab), carbohydrates, microbial biomass carbon (MBC), β–glucosidase activity, arylesterase activity, hidrofobicity and greenhouse gas (GHG) emissions (CO_2, N_2O and CH_4) at 0, 2, 4, 7, 15, 30 and 90 days of incubation. The first time-point was collected just after rewetting. The CT and MaW treatments were excluded in the analyses for Crec, Nrec, Clab and Nlab, since they had very low values, and experimental error could be higher than samples variability.

3.3 Soil and gas analyses

Soil pH and EC were measured in deionized water (1:2.5 w/v and 1:5 w/v, respectively); AS was determined by the method proposed by (Roldán, 1994); TOC, IC and Nt were determined by anelemental analyzer CNHS-O (EA-1108, Carlo Erba); Crec, Nrec,Clab and Nlab were determined by hydrolysis with H_2SO_4 (Rovira and Vallejo, 2000); the recalcitrance index for carbon (RCI = Crec / Corg) and nitrogen (RNI = Nrec / Nt) was calculated; carbohydrates were extracted in deionized water (1:5 w/v) and measured using the colorimetric method proposed by Brink et al. (1960) by addition of 0.2% anthrone in sulphuric acid; MBC was determined using the fumigation-extraction procedure after extraction with 0.5 M K_2SO_4(Vance et al., 1987). The non-fumigated fraction was considered as Csol; β-glucosidase activity was determined according to Tabatabai (1982), arylesterase activity was measured according to Zornoza et al. (2009);the hidrophobicity was assessed by the water drop penetration time test (Wessel, 1988).

GHG emissions were measured as the amount of CO_2, N_2O and CH_4evolved from 2 g of soil in 25 mL glass vials closed with crimp caps after 24 h incubation at 22 ºC using a gas chromatograph(AGILENT 6890N).

3.4 Statistical analyses

The fitting of the data to a normal distribution for all properties measured was checked with the Kolmogorov-Smirnov test at $P < 0.05$. Data were transformed using logarithms to assure normal distribution. A one-way repeated measures ANOVA was carried out for all properties independently for each sampling date to assess differences among treatments. Histrograms of the residuals from ANOVA were plotted for each variable to confirm that the normality assumption was plausible. When the null hypothesis was rejected, the separation of means amongst levels was made according to Duncan at $P< 0.05$. Relationships among properties were studied using Pearson correlations. Statistical analysis was performed with the software IBM SPSS Statistics 20.

4. RESULTS AND DISCUSSION

4.1 pH and electrical conductivity

All amendments were able to significantly ($P < 0.001$) increase pHowing to their alkaline nature (Fig. 1A).The sampleswith marble wasteshowedthe highest values (7.76-8.25), confirming that MaW is an effective amendment for pH neutralization, also observed by previous authors (Janjirawuttikul et al., 2011; Tozsin et al., 2014a; Zornoza et al., 2013).

EC only significantly decreased ($P < 0.001$) with regard to CT in the treatments containingMaW, with an average value of 4.21 dS m^{-1} at the end of the incubation (Fig 1.B). The combined addition of biochar with MaW showed significantly higher EC than the treatment that only received MaW, likely due to the presence of soluble salts in the biochar (Zornoza et al., 2016), which can be incorporated into the soil. Increases in EC after addition of biochars derived from different sources have been previously reported owing to the input of soluble salts (Burrell et al., 2016; Molnár et al., 2016). Thus, the decrease in EC was a direct effect of the addition of calcium carbonate, since Ca^{2+} can react with soil sulphates (which can derive from oxidation of pyrite, galena, sphalerite, etc) and form mineral precipitates such as $CaSO_4 \cdot 2H_2O$, which can reduce the amount of soil soluble sulphates (Fernández-Caliani and Barba-Brioso, 2010). The negative correlation between IC and EC supports this fact ($r= -0.89$; $P< 0.001$). The increase in pH can also promote the precipitation of different ions in the soil. In fact, the negative correlation found between pH and CE supports this hypothesis ($r= -0.82$; $P< 0.001$).Although decreases in EC are not essential to contribute to soil formation, they are positive to facilitate the colonization and growth of microbial and plant communities. However, salinity is still high in the Technosol created with the addition of MaW; so, only salt tolerant microorganismsand plant species would satisfactorilygrow(USDA, 1999).

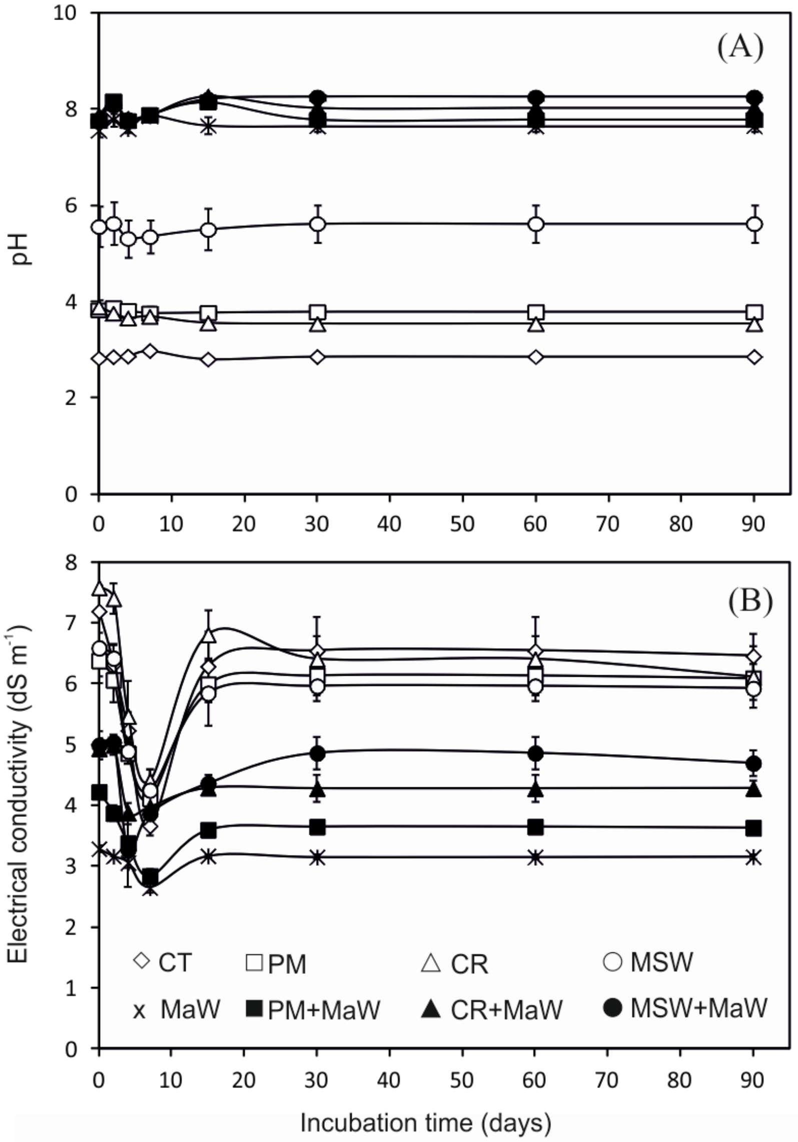

Figure 1. Evolution of pH (A) and electrical conductivity (B) in the unamended mine residue and Technosols created with different amendments during 90 days of incubation. Error bars in each sampling date denotes standard deviation (n = 3). CT: control (unamended mine residue); PM: pig manure-derived biochar; CR: crop residue-derived biochar; MSW: municipal solid waste-derived biochar; MaW: marble waste.

4.2Carbon and nitrogen dynamics

IC was also stable during the entire incubation in those samples receiving MaW, with values ~ 20 g kg^{-1} (data not shown), promoting the maintenance of high pH in soils, with significant positive correlation between both properties (r=0.72; P< 0.001). TOC significantly increased in all treatments receiving biochar with regard to CT and MaW, with an average value of 18 g kg^{-1} (Fig. 2A). TOC remained stable at this level during the incubation in all samples, which was the organic carbon added with the biochars. Thus, there was no significant loss of organic carbon in any sample receiving biochar, confirming the high stability of the biochars. In fact, RCI was high in all treatments receiving biochar (Fig. 2B), with values > 0.70. CR-derived biochar, alone or in combination with MaW showed significantly lower RCI (0.70-0.80) than the rest of treatments (0.95-0.97). Clab increased during the first 7 days of incubation in all treatments (Fig. 2C). From that day, Clab slightly decreased and maintained stable during the incubation. Clab was higher in CR-derived biochar, alone or in combination with MaW, than in the other treatments was during the incubation. Csol followed the same trend than Clab, with increases up to day 7, to start at that date a decreasing trend (Fig. 2D). However, there were no significant differences among treatments with regard to Csol.Carbohydrates content was below detection limit in all samples. Thus, these resultssuggest that water-soluble organic compounds provided by biochar are scarce and do not incorporate into the soil. In addition, many soluble organic compounds can be adsorbed in biochar surfaces, and act and cement agents to form aggregates (Liang et al., 2010), and so no increase is detected in soil. Contrarily to our findings, Wang et al. (2016) observed that biochar addition to agricultural soils could increase Csol derived from native SOM, being this increased < 1% of total biochar C; however, this effect cannot be expected in mine soils with practically null native SOM. Thus, biochar can act as an amendment to increase stable organic carbon in soil, favoring carbon sequestration, with low incorporation of labile and soluble compounds.

Nt followed the same trend than TOC (Fig. 2E), with significant increases ($P < 0.001$) in all treatments receiving biochar with regard to CT and MaW, with an average value of 1.02 g kg^{-1} (Fig. 2F). RNI showed no significant differences among treatments receiving biochar, with values ranging from 0.81 to 0.97. These results suggest that most nitrogen provided by biochar is included in recalcitrant organic compounds, with low availability. RNI showed a negative significant correlation with RCI ($r= -0.71$; $P< 0.001$), suggesting that those soils with higher recalcitrant nitrogen compounds are related to lower recalcitrant carbon compounds. Nlab showed very low values (< 0.35 mg kg^{-1}) and high variability, with no significant differences among treatments (Fig. 2G). C/N ratio increased with addition of biochars from 3.8 to ~18.0, with no significant differences among samples receiving biochar (data not shown). This trend confirms the stabilization of organic matter in the Technosol, an essential process for soil creation. No sample showed hydrophobicity at any sampling time (data not shown). Although some biochars can become hydrophobic, those produced at high temperatures like in this experiment lose their hydrophobic compounds (Zornoza et al., 2016b).

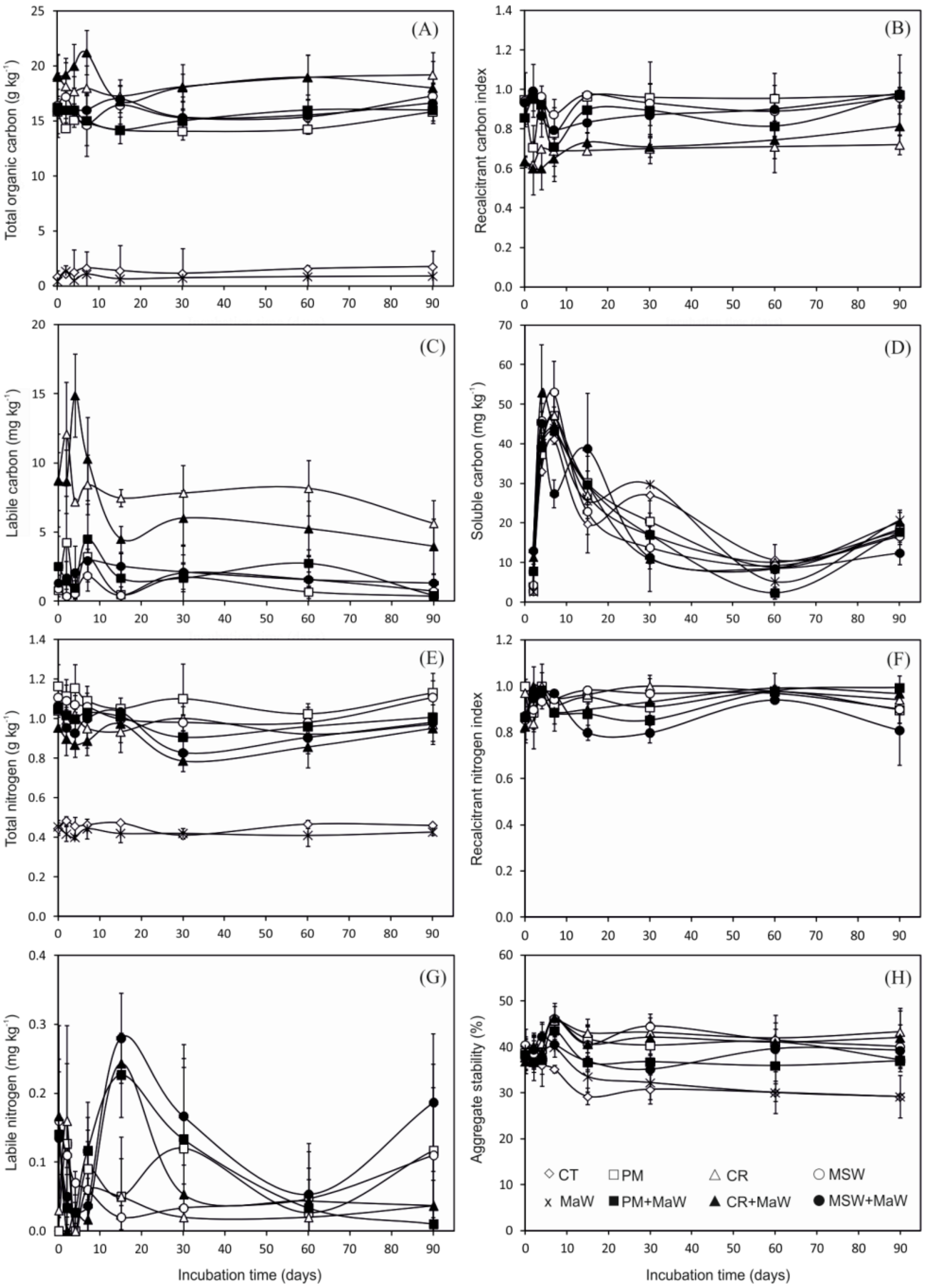

Figure 2. Evolution of total organic carbon (A), recalcitrant carbon index (B), labile carbon (C), soluble carbon (D), total nitrogen (E), recalcitrant nitrogen index (F), labile nitrogen (G) and aggregate stability (H) in the unamended mine residue and Technosols created with different

amendments during 90 days of incubation. Error bars in each sampling date denotes standard deviation (n = 3). CT: control (unamended mine residue); PM: pig manure-derived biochar; CR: crop residue-derived biochar; MSW: municipal solid waste-derived biochar; MaW: marble waste.

4.3Aggregates stability

The different biochars significantly increased (P < 0.001) soil aggregate stability with regard to CT by ~40% (Fig. 2H). This increase, not observed with the addition of MaW alone, appeared after 7 days of incubation, and values were practically stable up to the end of the experiment, with no significant differences among the treatments receiving biochar. Biochar acts as a binding agent with minerals, organic matter and microorganisms and thus promoting the formation and stabilization of macro-aggregates (An et al., 2010; Jones et al., 2010). In addition, biochar surface can have labile organic compounds which may act as substrates for microorganisms which, in turn, may build further aggregates though the excretion of mucilage or development of fungal hyphae (Steinbeiss et al., 2009; Liang et al., 2010). It is important to highlight that increases in AS were found after a decrease in Clab and Csol, which may be stabilized by its interaction with mineral particles, or also consumed by microbial populations.

The combined addition of biochar with MaW had no effect on AS. Zanuzzi et al. (2009) concluded in acidic mine residues amended with pig manure and sewage sludge that the addition of calcite was recommended to stabilize soil organic matter and promote the development of soil structure, since the Ca^{2+} bridge with organic compounds favors the formation of stable aggregates. However, since the stabilization of organic matter is needed to increase water-stable macroaggregates (Herath et al., 2013, Zornoza et al., 2016a), it seems that the addition of biochar, with high recalcitrant organic matter, can contribute to increase AS with no extra addition of Ca^{2+} in acidic mine soils. In fact, AS was significantly correlated with TOC (r=0.63; P< 0.001), Nt (r=0.52; P< 0.001), Crec (r=0.54; P< 0.001) and Nrec (r= 0.49; P< 0.01), confirming that the stable organic matter added with biochar was responsible for increments in the AS. Zornoza et al. (2016a) also observed that there was a significant positive relation between soil recalcitrant carbon and aggregate stability in reclaimed mine soils with biochar.

4.4Microbial biomass and enzymeactivities

Biochars significantly increased MBC during the first 7 days with regard to CT (Fig. 3A). However, from this date, there were no significant differences among treatments any longer, with MBC content similar in amended and control samples. This pattern was similar to that observed with Csol (Fig. 2D), suggesting that microorganisms started growing with the presence of easily-available organic substrates (Pérez de Mora et al. 2005), which were rapidly depleted or stabilized after 7 days. Biochar was not able to provide further available substrates for microbial development, and microorganisms size could not increase.

β-glucosidase activity was below detection limit in all samples during the entire incubation. This suggests that microorganisms are not releasing this enzyme related in the hydrolysis of glycosides and cellobiose to obtain monosaccharides, likely due to the lack of free easily available carbohydrates provided by biochar. Some authors previously found that biochar addition can suppress labile organic compounds to enzyme degradation by adsorption on its surfaces (Kasozi et al., 2010; Zimmerman et al., 2011).

Arylesterase activity was more closely related to changes in pH than in organic carbon content. This is confirmed by the significant positive correlation between arylesterase and pH ($r= 0.94$; $P< 0.001$), and the lack of correlations with any organic fraction. Thus, those treatments that received MaW were able to highly increase the activity of this enzyme (Fig. 3B). Zornoza et al. (2009) and Renella et al. (2011) previously reported that arylesterase activity is highly sensitive to shifts in pH, with higher activity in basic soils.

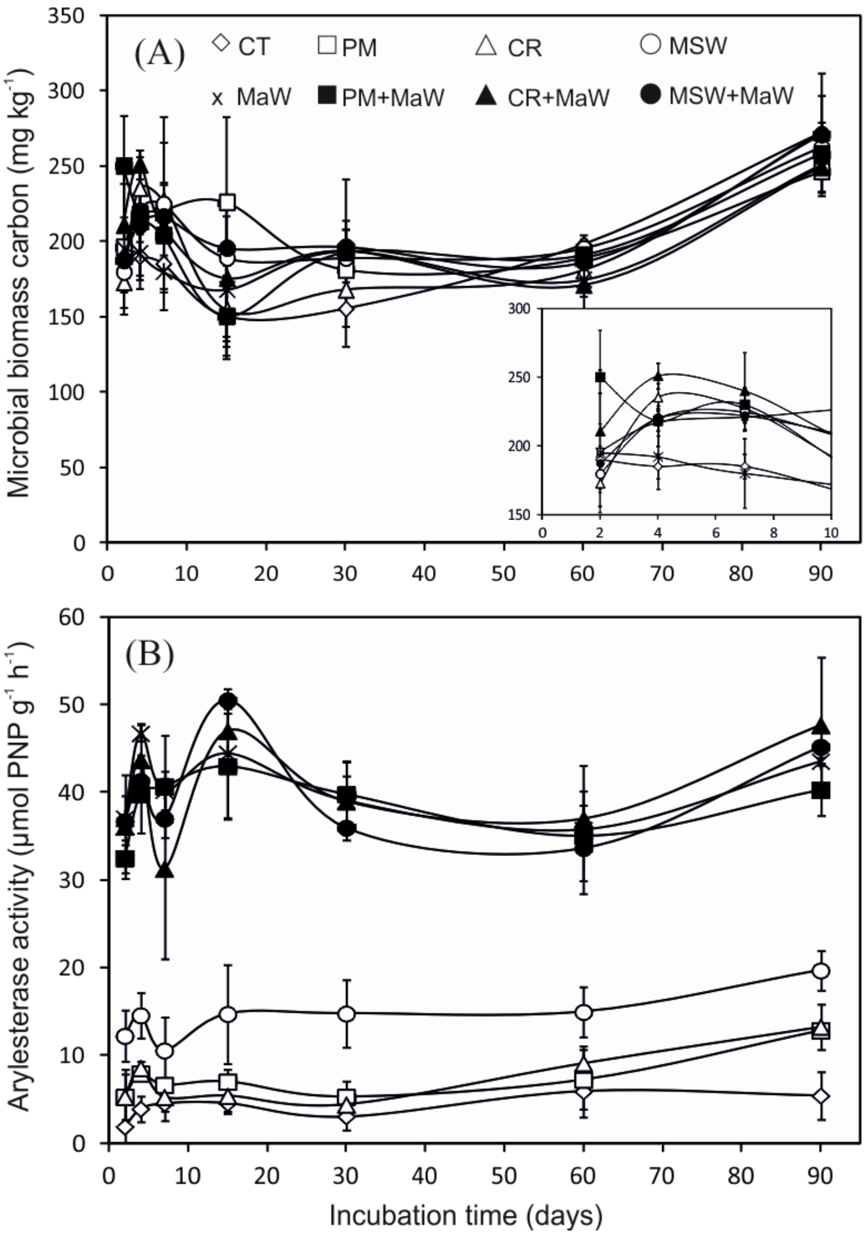

Figure 3. Evolution of microbial biomass carbon (A) and arylesterase activity (B) in the unamended mine residue and Technosols created with different amendments during 90 days of incubation. Error bars in each sampling date denotes standard deviation (n = 3). CT: control (unamended mine residue); PM: pig manure-derived biochar; CR: crop residue-derived biochar; MSW: municipal solid waste-derived biochar; MaW: marble waste; PNP: *p*-nitrophenol. Inset in top graph is an enlarged representation of the first 10 days of incubation to visualize shifts in microbial biomass carbon.

4.5Greenhouse gas emissions

Previous studies have shown biochar amendments to soil have the potential to reduce GHG emissions including CO2, ethane (CH4), and nitrous oxide (N2O) (Cayuela et al., 2010;

Scheer et al., 2011), this justified the behavior of our amendments at the end of the experimentation.

CO_2 emissions were not significantly affected by any amendment, with values similar to CT (Fig. 4A, B). N_2O emissions increased, as a general pattern,with addition of biochar(Fig. 4C). Increases were only significant for PM+MaW, MSW+MaW and CR during the first 30 days, and for CR and CR+MaW at the end of incubation. When the cumulative N_2O emissions are shown (Fig. 4D), it can be observed that CR,CR+MaW and PM+MaW significantly increased the cumulativeN_2O emissions with regard to CT by 16 mg kg^{-1}, 12 mg kg^{-1} and 10 mg kg^{-1}, respectively after 90 days. Thus, increased N_2O emissions were related to lower RCI. All soils receiving biochar significantly decreased CH_4 emissions from day 30 with regard to CT (Fig. 4E, F), with an average saving of 22 mg kg^{-1} in 90 days.

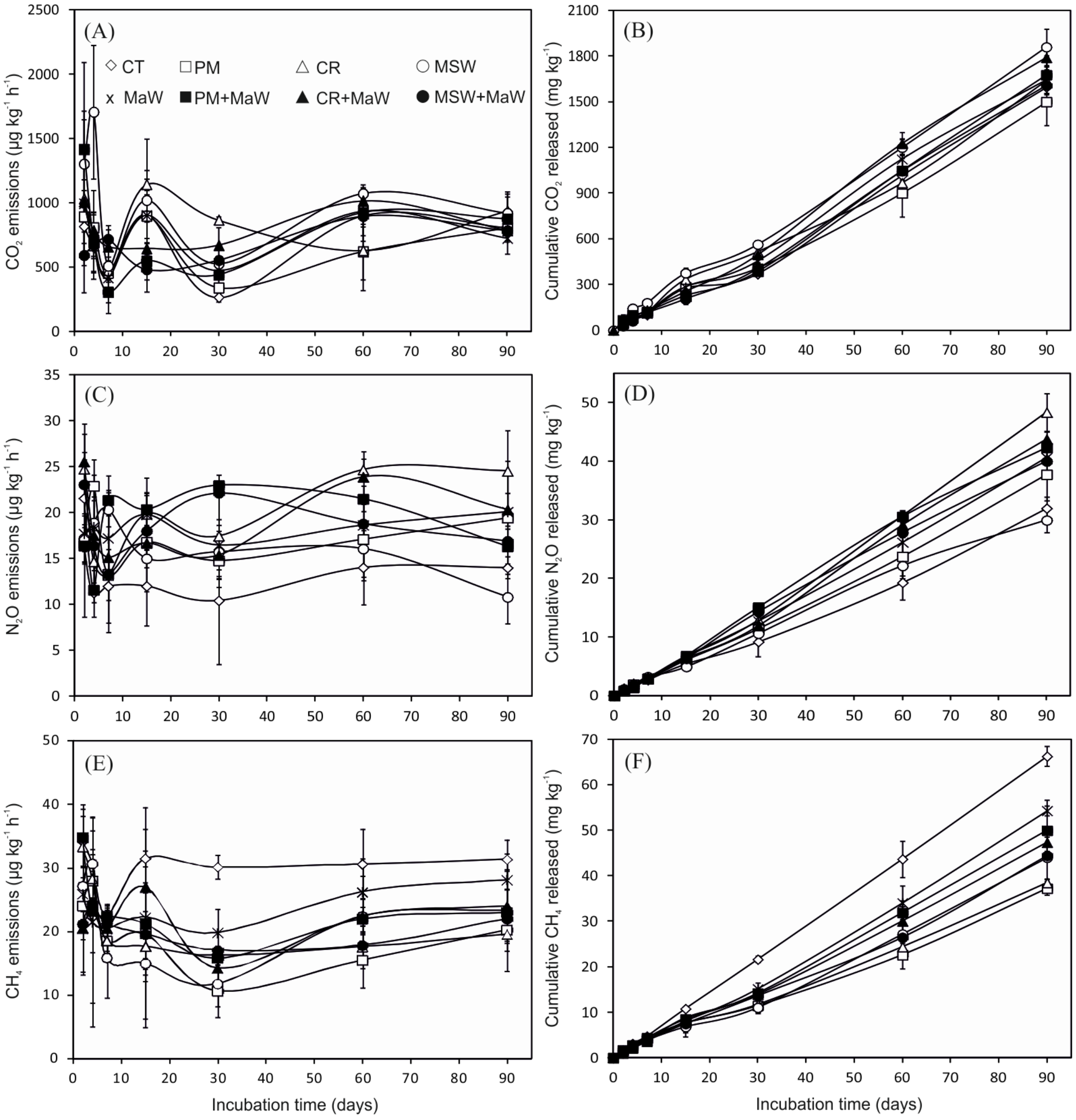

Figure 4. Evolution of CO_2 emissions (A), cumulative CO_2released (B), N_2O emissions (C), cumulative N_2O released(D), CH_4 emissions (E) and cumulative CH_4 released (F)in the unamended mine residue and Technosols created with different amendments during 90 days of incubation. Error bars in each sampling date denotes standard deviation (n = 3). CT: control (unamended mine residue); PM: pig manure-derived biochar; CR: crop residue-derived biochar; MSW: municipal solid waste-derived biochar; MaW: marble waste.

5. CONCLUSIONS

All the Technosols created with biochar, alone or in combination with marble waste, increased aggregate stability and soil organic carbon and nitrogen, with high recalcitrance indices. However, the labile and water soluble organic compounds provided with biochars were low to stimulate microbial biomass and activity. The only effect observed with the addition of marble waste was the increment and maintenance of pH around the target value, the decrease in electrical conductivity, and the improvement of the environment for arylesterase activity. No effect of marble waste was observed in any organic matter fraction neither aggregate stability. All Technosols created were able to reduce CH_4 emissions, with no effect on CO_2emissions. However, N_2O emissions increased with the addition of crop residue-derived biochar alone or together with marble waste, and with the addition of pig manure-derived biochar in combination with marble waste, related to lower recalcitrance index for soil organic carbon. These results suggest that biochar, produced by diverse sources, is an effective strategy to sequester carbon in soil and improve soil structure. However, to effectively reclaim mine residues, it would be necessary to add a labile source of organic matter to promote the development of microbial populations.

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ANNEX I: TABLES

Table 1.Main characteristics of the different residues and biochars used for the Technosol creation.

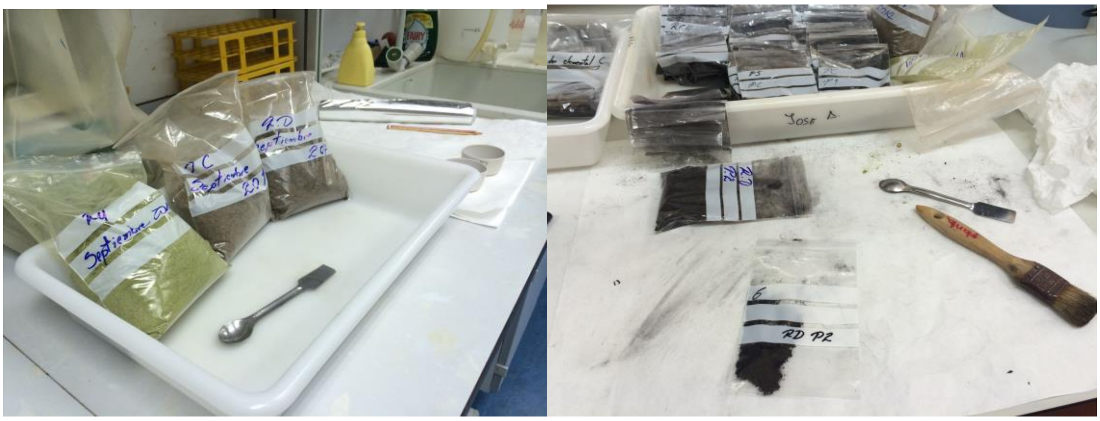
Residue[a]	pH	EC[b]	OC	N	Cu	Zn	Pb	Cd	Ca	Mg	Na	K	$CaCO_3$
		dS m^{-1}	g kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%
Mine residue	2.82	7.20				1030	6636	0.99	-	-	-	-	-
MaW	8.00	2.20	-	-	0.4	260	1.4	0.90	2190	347.00	69.02	59.02	98
PM	10.52	3.99	405	27	100.2	113	3.2	0.35	109	21.27	7.55	24.74	-
CR	10.77	15.89	480	23	16.7	82	10.3	0.10	88	21.01	2.60	68.66	-
MSW	9.78	8.41	288	13	130.6	412	132.1	0.79	142	11.96	13.30	17.98	-

[a] MaW: marble waste; PM: pig manure-derived biochar; CR: crop residue-derived biochar; MSW: municipal solid waste-derived biochar

[b] EC: electrical conductivity; OC: organic carbon; Nt: total nitrogen

ANNEX II: PHOTOGRAPHS

Source material used and obtained biochars



pH analysis

Stable aggregates analysis

Microbial Biomass Activity analysis

Green House Gases analysis

Mine residues used